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The position of the Le Chatelier-Braun principle as general criterion of stability

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Introduction

Although the term "equilibrium" is frequently encountered in almost every branch of science, the comparison of the different definitions formulated in Physics and some neighbouring sciences shows that not only are they incongruent, but that they often refer to different things to which the same name of equilibrium is given, even in the domain of Physics alone. The most striking feature is the inadequate distinction between equilibrium and its stability. It is also significant that whereas these questions were amply discussed by the classical authors of the XIXth century, our contemporaries are rather negligent in this regard although the position is by no means cleared. As a whole, the current state of knowledge of this fundamental problem of sciences must be estimated as quite unsatisfactory. A preliminary paper, intended for a wider circle of scientists is being published elsewhere.[1] The present, stricter treatment covers the field of Physics and physical Chemistry as it was not possible for the Author to extend such work to other sciences. The Author however feels that it may be done by competent scholars believing that it is just in the fields of other branches of science that the methods presented in this paper can be most helpful.

Our task is to compare critically the common features of the different existing definitions in order to reach the most general expressions. First of all let us emphasise that it hardly seems useful to connect equilibrium with absolute rest, as has often been done. We know from relativity, that a well defined *macro-state* of *absolute rest does not exist.* But even a state of rest relative to an arbitrary set of axes of reference cannot be regarded as an essential feature of equilibrium if we want to include steady motions performed by an ideal pendulum, planets and other simple mechanical systems such as shown below in examples. The *micro-state* is *never* one *of rest,* owing to heat-motions and subsequent fluctuations, so that in many cases the equilibrium has a statistical character.

Thus we may propose to regard a system[2] as being in *equilibrium* when it is *stationary* viz. when its state of motion or rest does not change.

As in reality every existing system is bound to be disturbed from outside, we must naturally be interested not only in the bare fact of existence of equilibrium, but also in its *stability* which can be defined as the ability of *maintaining equilibrium against external interference.*

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[1] Z. KLEMENSIEWICZ, Sur une définition générale d'équilibre et de stabilité. Scientia 1949.

[2] We use the term "system" in the sense of HELMHOLTZ and GIBBS, to denote the physical object or ensamble of objects of interest.

In the domain of Physics we can discern a formulation referring to the *conditions* of *equilibrium*, which we shall designate as *variational* definition and another, concerned with the conditions of *stability*, designated as *operational* definition.

Variational definition

This definition can be traced back to JOHN BERNOULLI's principle of virtual displacement, originally limited to conservative mechanical systems but afterwards extended by GIBBS into the field of Thermodynamics. We affirm that it can be still further usefully generalised.

Thus we consider a system to be then and only then in equilibrium, when a determining function remains invariant to *infinitesimal* virtual[1] changes of the parameter, the consequent changes of the function being small of a higher order. This can be expressed mathematically either in the form:

$$\delta \Phi = 0 \tag{1}$$

or

$$\Phi = \text{extr.} \tag{2}$$

Φ being the determining function.

The conditions (1) and (2) are often considered as equivalent although there are singular but important cases in which only one of them can be valid. The nature of the function Φ must be interpreted in every case, using the laws governing the given system. In Mechanics it means *potential energy.*

In thermodynamical systems it can be interpreted, accordingly to conditions as a *function of state* such as internal energy, enthalpy, Helmholz's free energy, thermodynamic potential or entropy. These scalar quantities have the dimensions of work, except for entropy.

Chemical equilibrium can be dealt with on the same lines, mainly with thermodynamic potential as determining function.

We may further be tempted to regard a ray of light, passing through an optical medium, as a system in equilibrium. In this case the optical length of path would be the determining function, having an extremal value, according to Fermat's principle.

As there may be still other cases where an entity, not having the dimension of work, acts as determining function, I replaced the term "work" in the usual formulation of Bernoulli's principle by the more general term "determining function". Its meaning in conditions (1) and (2) is to be deduced in every case from the laws, established in the given branch of science.

Operational definition

The variational definition is concerned with the mere existence of equilibrium as such but does not tell us anything about the kind of its stability. From the mathematical point of view we could discern between a minimum and a maximum of a determining function on the basis of the (+) or (—) sign of the second derivative. But this method being purely local does not enable us in principle to foresee the behaviour of the system in the case of *finite* disturbances which are likely to occur. What we are interested in, is not so the kind of extremum relatively to the immediate neighbourhood but the trend over a wider area. In the case of a finite displacement of the coordinate the change of the function is not zero, but has in general a finite value, which can be positive or negative. This is the starting point of the *operational definition.*

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[1] Viz. imaginary changes, compatible with conditions imposed to the system (constraints).

There is a well known prescription that in order to distinguish between stable, indifferent and unstable systems, we have to perform the following, experimental in principle, operation. We change one of the parameters by external action and watch the behaviour of the system. It returns to the original position, after the interference ceases, if it is stable, it changes further if it is instable. In the limiting case of indifferent equilibrium the system does not move at all from itself. So in order to determine the sign of stability we must disturb the equilibrium. This operation enables us moreover to distinguish between a state of *true equilibrium* and the one of motion, slowed down by *frictions*, except of course in the case of indifferent equilibrium. If the sign of the disturbance is reversed, the sign of the reaction is inverted too. But it does not refer to the variation of the determining function, if it is a scalar quantity.

As the actual execution of the aforesaid operation is possible or desirable in exceptional cases only, theoretical criteria have been sought and found in some cases. For *simple mechanical* systems it follows e. g. from Hamilton's principle not only that Φ in (1) means potential energy, but moreover that the extremum in (2) must be a *minimum*:

$$\delta_2 \Phi > 0. \tag{3}$$

Likewise it can be deduced from the principles of Thermodynamics that, accordingly to the conditions, stable equilibrium of thermodynamical systems is connected with a *minimum* value of internal energy, enthalpy, free energy, or thermodynamic potential but, on the contrary, with a *maximum* value of entropy. It is obvious that we can only formulate such conditions while in possession of a full knowledge of the laws governing the given system. Unfortunately we are not always in this favourable position.

Principle of Le Chatelier-Braun. Historics

We will try to show that in such cases and in a general way, the principle introduced by LE CHATELIER[1] may be very helpful. Although it was conceived as a qualitative generalisation of the formulae of CLAPEYRON-CLAUSIUS and VAN t'HOFF and defined by Le Chatelier himself as a formulation of the laws of chemical equilibrium, it proved to be far more *general.* The applications quoted in L. Ch. paper cover the domain of Chemistry, physical Chemistry and many parts of Physics. The paper also deals with cases of irreversible processes, local changes and differences of temperature and pressure and metastable states. The demonstration is however inductive by way of examples only and the formulation rather complicated and not sufficiently precise. A comparatively restricted version was given independently by BRAUN[1] so that the doctrine has been known as the principle of Le Chatelier-Braun. CHWOLSON gave a very clear exposition of it[2] with a hint of its applicability in biological sciences. This afterwards lead to teleological formulations. Instead BENEDICKS[3] rightly emphasised the view that the principle may be regarded as *criterion* of *stable equilibrium.* His work was the starting point for the present paper. Again EHRENFEST[4] and eventually PLANCK[5] attempted to give to the principle a mathematical form and, developing an idea of BRAUN, arrived at a formulation of *different content.* The entanglement of the two versions and the belief that the Le Chatelier-Braun principle yields only a qualitative result which, in some cases, could be deduced quantitatively from thermodynamics, have contributed to the loss of credit of the original principle. We will not commit ourselves, in this paper, to a further investigation of the Ehrenfest-Planck heresy but wish to show what profit can be derived from the orthodox formulation.

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[1] LE CHATELIER, C. r. *99*, p. 786 (1884).

Formulation and demonstration of the principle

Let us assume that our system is separated and its *macro-state* defined by a set of optional parameters.[6] Between them some relations may exist such as geometrical constraints or equation of state. The number of such constraints is supposed to be less than the number of parameters, so as to leave to the system at least one degree of freedom. The fact that the principle can only be valid for systems which are *free to move*, was clearly realised from the beginning. Thus it was often referred to as principle of mobile equilibrium. We then imagine one free parameter altered by an external interference and we examine the changes the system is undergoing as a result of this interference. Then three cases are possible:

1. The system *obeys* the principle. It means that such changes are generated within the system which *oppose* the external interference and endeavour to restore the original position. Such a system remains steadily in equilibrium, so we will call it *autostatic,* following a proposal of Braun.
2. The system *disobeys* the principle. The changes are such as to *reinforce* the external action so that further displacements of the same sign occur and move the system away from its original state. Let such a system be called *contrastatic.*
3. Finally a *limiting* case may be thought of, in which *no further changes* occur when a parameter is changed from outside. The case is that of indifferent equilibrium and the system remains in that sort of equilibrium, regardless of the external,

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[1] BRAUN, F., Zeitschr. f. phys. Chemie *1,* p. 259 (1887).

[2] CHWOLSON, Textb. of Physics, Vol. III.

[3] BENEDICKS, Zeitschr. f. phys. Ch. *100,* p. 42 (1922).

[4] EHRENFEST, ibid., *77,* p. 227 (1911).

[5] PLANCK, Ann. Phys. *19,* p. 759 (1934).

[6] Many mistakes have arisen, in the past, when the relations between the considered system and the environment were not clearly defined. We shall refer to a system as "open" or "closed" depending on it being able or not to exchange matter with the neighbourhood. In the present paper we are dealing with the latter only. We call a system "isolated" if any exchange of energy is impossible. If one parameter only can be changed by external interference, the system is referred to as "non-communicating". In such a system all remaining parameters are "left to themselves" viz. allowed to change only according to the internal constraints. If another parameter is to be "kept constant"; a further external interference, through exchange of work or energy, is necessary. Such a system is called "communicating".

positive or negative, displacements of the parameters. Such systems are commonly called *astatic.*

Briefly said, an outside interference generates either changes which are opposite or such which are conform or, finally, no changes at all. The first case is that of a stable, the second that of an unstable and the third that of an indifferent system. *The orthodox formulation of the Le Chatelier-Braun principle states that the first kind of behaviour is general.* That this must be true in nearly all actual cases, will be shown below.

In this way the operational definition of stability of equilibrium is found to be naturally connected to the Le Chatelier-Braun principle.

The three cases could be also designated as positive-stable, negative-stable and 0-stable.

It would seem a priori that a given system could display positive stability for the changes of one of its parameters and negative stability for changes of another. Actually such a possibility appears restrained by reasons explained below. On the other hand it is certain that systems can be stable for *limited* external interference and become instable beyond this limit. We will call them *imperfectly* autostatic.

Having defined the imaginable kinds of systems, we may now ask which of them and under what conditions are likely to be present in Nature. If we realise the many different *macroscopic disturbances* occurring *in the Universe* e. g. gravitational, radiative perhaps also magnetic and electric actions of celestial bodies, tectonic motions, meteorological factors, actions of living beings and also taking into consideration *microscopic disturbances* viz. disordered heat motions and consequent material and radiative fluctuations, we must conclude that *contrastatic systems can only have a very restricted lifetime.* As the limits for astatic systems are ideally narrow, we can conclude that *of all systems in equilibrium according to (1) or (2) only autostatic ones are actually present in Nature.*[1] Also, if a system is to survive, it must be autostatic for changes in all parameters which are likely to be disturbed. Henceforth nearly all actually encountered systems are autostatic for changes of any parameter. So that if a priori the Le Chatelier-Braun principle can claim validity for one only class of systems, viz. those in stable equilibrium, it proves *actually valid for most existing systems.*

But we should clearly state that there is *no need to admit the teleological conception* viz. *that Nature does reveal a special tendency to create and to maintain stable systems.* The a priori probability of generation is equal for all possible systems, but unstable ones have little chance of survival. In this way an apparently teleological principle proves once more to be that of natural selection. This *biological* principle is independent of any laws of Physics and proves useful over a very wide field. It has been already tacitely admitted in the theory of nucleus. It can still be usefully generalised.

If, in spite of this, unstable systems seem to be found not so very seldom, the answer is that they belong in fact to one of the following classes:

1. *Imperfectly* autostatic systems, as defined before. This is the case of numerous objects, we are hadling in every-days life. In Nature we can observe many such systems, as they exist for a time and eventually break down, under the impact of a major disturbance.

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[1] This has been already noticed by OSTWALD, Vorles. üb. Naturphil. 3 Aufl. 1905, p. 247, without the reasons being given. But see the 2nd paragraph on next page.

2. Contrastatic systems, strongly *damped.* These are *not in true equilibrium* but change very slowly, owing to *frictions* of different kind. Such frictions do, of course, also occur in disturbed autostatic systems and prevent them from returning to their original positions, making it difficult to ascertain the true nature of equilibrium. Hence difficulties encountered in research of equilibria in solids, such as alloys, rocks, concrete etc. Also great care is needed in connecting states of metastable equilibrium with relative extrema.

We should also draw attention to a particular class of systems viz. able to keep *automatically* the level of indifferent equilibrium (s. Ex. 9 ff). We may call them *autoastatic.*

If the Le Chatelier-Braun principle is primarily used to ascertain if a given system, sufficiently known, is stable, the question may be also reversed. When we have to do with an unexplored system and find by experience that it is autostatic, we can draw conclusions about the nature of acting forces.

Examples

We will give here a few examples of the most typical cases in order to demonstrate the essence of the L. Ch.-B. principle. Most of them are familiar to physicists and physicochemists, but I tried to emphasise some important points which have been often overlooked or even wrongly interpreted. For more examples see references on p. 295 and 296.

Ex. 1. A heavy mass resting at the bottom of a perfectly smooth concave surface, supposed for the sake of simplicity to be one of revolution around the z-axis, is in stable equilibrium. When it is displaced to the side a gravitational component R tends to restore the original position. Then

$$dR = -\, m g \varphi(r)\, dr. \tag{4}$$

For an infinitesimal, virtual displacement viz. following the slope of the cavity, the change of potential energy is small of a higher order according to (1). The determining function being the potential energy, depends on the parameter r i. e. the distance of the masspoint from the axis of revolution

$$d\Phi = -\, m g f(r)\, dr. \tag{5}$$

In general if there is a point bound to move along a curve in a field determined by a potential Ψ, we have

$$d\Phi = -\, \Psi f(r)\, dr. \tag{6}$$

In the case of a *conservative* system, the energy gained, due to the finite displacement, must manifest itself in a steady periodic motion about the original position, after the disturbing force ceases to act. This is a very simple case of vibrations about equilibrium configuration.

For *dissipative* systems, e. g. an arrangement as before, dipped in a viscous fluid, the vibrations are damped and the system returns eventually to its original position, while the kinetic energy is converted into heat. The work performed by external forces in order to displace the body by a given amount, depends on the velocity of change. It tends towards a minimum with the velocity tending towards zero.

This minimal work is the same as that required, caeteris paribus, in a conservative system.

Ex. 2. Same body on top of a convex surface, illustrates the case of *unstable* equilibrium. Displacement yields a component pointed in the same direction as the disturbing force. Thus if such a system is disturbed, a steady transit of potential energy into kinetic form follows and the motion is directed away from the original position. In a dissipative system the increase in the kinetic energy is limited, the energy of ordered motion being increasingly changed into heat.

Ex. 3. Same sphere on a horizontal plane is *astatic*. It remains unaffected by any displacement because no force whatsoever is generated. The potential energy remains constant and there is no transit into kinetic form. If the system is dissipative, the work done by the external force is directly transformed into heat.

In all three cases of stability we have evidence of an invariant extremal value of the potential energy, acting as determining function, according to (1) and (2). Though for the singular case of a conique surface only the condition (2) is satisfied.

Ex. 4. An elastic body, deformed by an outside force, generates an elastic force, opposing the external influence. The variations of the elastic force are of the same order as the variations of the displacement just as in the case of a conique surface. But if the energy of deformation, which is a quadratic function of the displacement, is taken as the determining function, it fits both (1) and (2).

Ex. 5. The case of elastic properties of a perfect gas is alike, the internal pressure opposing the external interference. However, it differs notably in the respect that, while in the case of a solid body internal work predominates, with a perfect gas external work only is to be done. It means that some source of external pressure, acting upon the piston, must be included in the system. For a gas, free to extend alone, neither of the conditions of equilibrium is satisfied and there can be in fact no position of equilibrium.

Ex. 6. Another effect which accompanies changes of volume is the thermal one. Most bodies have a positive coefficient of thermal expansion and accordingly they generate heat when compressed and absorb when expanding. But a body with a negative thermal expansion e. g. water below 4° C[1] or strained rubber, shows the opposite behaviour. We shall thus conclude that the mechanical (as in ex. 4) and the thermal effects of a change of volume are, to same extent, independent. Water below 4° C will resist compression although it absorbs heat when compressed. Plastic materials will not, although they generate it.

In the foregoing examples we have always assumed that the system remains unaltered but for one parameter which is changed by external interference. Now during adiabatic compression changes of volume are accompanied by changes of temperature so that such properties of the body as elastic constants must alter. Yet even such complicated relations are ruled by the principle of L. Ch.-B.

Ex. 7. Surface layers may be treated as 2-dimensional gaseous systems. The surface-energy, a product of surface-tension and area, has the character of potential energy. In the absence of other forces equilibrium is not reached until the free surface area drops to a minimum compatible with the volume of the liquid. The surface-tension can be greatly reduced by the addition of certain bodies or slightly increased by the addition of others. The reason is that bodies of the first kind, decreasing the surface-energy, will gather in the surface-layer and can reach there high concentrations. Bodies of the second kind must desert the surface so their influence is weak. A quantitative formula, deduced thermodynamically by Gibbs is:

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[1] R. W. BRIDGMAN, Proc. Amer. Ac. *47*, p. 439 (1912).

$$S = -\frac{c\,d E_s}{RT\,d c}. \tag{7}$$

S being the excess of the body in the surface-layer, c its concentration in the bulk of the liquid, E_s the surface-energy.

Ex. 8. Electromagnetic systems are closely related to the mechanical ones.

A special case of the Le Chatelier-Braun principle, the qualitative law of magnetic induction was formulated by LENZ[1] as early as 1834. A modernised version of it reads: "the direction of induced EMF is such that it tends to oppose the change to which it is due".

The interesting feature of this case is that, as in the case of a damped mechanical system, time is involved. The qualitative expression for the E.M.F. is:

$$V = -\frac{dN}{dt}. \tag{8}$$

But there is an important difference between the two cases. Whereas a mass-point has a defined energy in a gravitational field even when at rest, a conductor at rest in a magnetic field has none. So the case of unstable equilibrium for electromagnetic induction is ruled out by a mere application of Thermodynamics without reference to the biological principle.

In thermodynamical systems there can be no overrunning beyond the position of equilibrium as these systems are unable to store kinetic energy of ordered motion reversibly. A reversible change in these systems can only be quasi-stationary i. e. infinitely slow. Thus conditions of equilibrium are those of reversible changes.

The following examples form a distinct group as they refer to *polyphase* systems which as pointed out before would be auto-astatic, for a wide range of isothermal changes of volume at constant pressure.

Ex. 9. Influence of the temperature on the vapour-tension of liquids. The liquid phase is in equilibrium with its saturated vapour for an 1-dimensional continuum of pairs of conjugated values of T and p, forming a plane curve, between the triple and the critical points. If T were raised from outside, the liquid would evaporate entirely if the vapour was free to escape. But as the system is supposed to be closed and non-communicating, the pressure rises simultaneously and results in a displacement of equilibrium along the boundary curve, to a point with higher values of T and p.

A change of volume at constant T involving evaporation or condensation under pressure which remains also constant, no external work is spent or gained but sources or sinks of heat must be provided, to supply or absorb the latent heat. The determining function in such cases is Gibbs function, as it has the same value for liquid and gas along the boundary curve. So it does satisfy the conditions (1) and (2) and there is 0-stability.

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[1] LENZ, Pogg. Ann. *31*, p. 483 (1834); *34*, p. 385 (1835).

We are interested, more often, in phenomena in which both temperature and pressure change. These changes are interdependent and the resp. formulae are easily won by applying the laws of Thermodynamics to cyclic processes in which a given mass of substance is reversibly transferred from one phase to another, between two temperatures. The well known Clapeyron-Clausius formula for saturated vapour-pressure belongs to this category:

$$\frac{dp}{dT} = \frac{L}{T(V_g - V_l)}. \tag{9}$$

Here too neither of the variables can be regarded as a determining function, satisfying the conditions (1) and (2) as their changes are of the same order of magnitude. The more general principle of L. Ch.-B. still *holds as criterium* of stability, independently of the choice of parameters.

Ex. 10. The dependence of the vapour-tension upon pressure other than the pressure of the vapour itself, e. g. that of a foreign gas, insoluble in the liquid, is very simple to explain. The rise of pressure on the liquid raises the vapour-tension, because through evaporation the liquid escapes compression. A thermodynamical formula has been deduced by Poynting:

$$\left(\frac{dp}{dT}\right)_T = \frac{V_0(1 - \alpha P)}{v} \tag{10}$$

where P is the pressure over the liquid, V_0 its molal volume at $P = 0$, v the molal volume of the saturated vapour and α the coefficient of compressibility of the liquid, all values taken at constant T.

Ex. 11. On the same lines may be treated the displacement of the melting point through rise of pressure exerted upon the solid phase only. The melting point is always decreased, but only in a non-communicating system is equilibrium possible.

When both phases are exposed, the thermodynamical formula is similar to (9)

$$\frac{dT}{dp} = \frac{T(v_l - v_s)}{F} \tag{11}$$

the latent heat of fusion being always positive, the sign of the derivative depends on whether the specific volume of the liquid is higher or lower than that of the solid.

Ex. 12. The case of the dependence of solubility on p and T is quite similar, except that the latent heat of solution may be sometimes negative. It is interesting to note that it was precisely the study of solubility which suggested to both, Le Chatelier and Braun, the idea of the principle.

Ex. 13. The displacement of a chemical reaction with changes of temperature and pressure is to be understood in analogy to ex. 9 although the system is monophase. The rise of p favours reactions connected with a diminution of volume. Hence reactions of dissociation are advanced by a drop of pressure. The rise of T favours reactions leading to heat absorption and vice versa. The thermodynamic formula of Van t'Hoff, well known as isochore equation is:

$$\frac{d \ln K_c}{d T} = \frac{Q}{R T^2} \qquad (12)$$

where K_c is the constant of chemical equilibrium, Q the heat of reaction.

In the realm of natural sciences many geological examples may be found by Rastall[1]. These are in fact cases of examples 11—13.

The quantitative aspect

Some scholars believed that it would be possible to find a general quantitative form of which such formulae as (9), (11) and (12) would prove special cases. This is not my opinion. The L. Ch.-B. principle is *essentially* qualitative. The negative sign in (4), and (7) shows the opposite direction of the reaction. But where scalar quantities are involved, the sign depends on the adopted conventions. So is it negative in the mechanical formulae (5) and (6). It is positive in expressions (9)—(12) if thermodynamical convention is applied and negative with the thermochemical convention. The functional shape of the quoted formulae is rather an expression for the constraints of the system, which may vary. We can see it best in the case of equation (6) which is already very general. The function $f(r)$ gives the shape of the surface on which the mass-point is supposed to glide. The thermodynamical formulae (9), (11) and (12) will, when slightly transformed and integrated, contain an exponential term, indicating the statistical character of the equilibrium and its connection with heat-motions. It would be unwise to overestimate the usefulness of quantitative formulae. They are differential equations, containing several material-coefficients, which cannot be treated as constant, except in a narrow interval. Even in the simple mechanical case (4) g is not strictly constant. General integration is possible only after a thorough theoretical and experimental integration such as done by Nernst in application of his theorem. But the main profit we can derive from the L. Ch.-B. principle is just in domains which are insufficiently known.

Stabilisation

Systems which would be contrastatic by themselves, can often be *stabilised* by additional devices, either natural or artificial. The action of such stabilisers can be more (or less) prompt. Thus oscillations may result.

Ex. 14. An electric conductor with a positive coefficient of conductivity e. g. a carbon filament lamp, connected to a source of constant EMF, forms basically a contrastatic system. If the EMF rises, the current and the heat supply increase with a consequent rise of temperature causing decrease of resistance and a further increase of temperature and so forth. At the same time, however, increasing temperature brings a steep rise of radiated energy which outweighs the growth of electric conductivity and prevents a further rise of temperature. So it is possible to use carbon filament lamps, within suitable limits of EMF. But an adiabatic system of this kind would be hopelessly contrastatic. Fluctuations of the EMF are also enhanced by such resistors. On the contrary, resistors with negative coefficients are autostatic by themselves and can be used as stabilisers.

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[1] Rastall, Physico-chemical Geology.

Ex. 15. Mechanical and electrical industries offer numerous examples of artificial stabilising devices.

Ex. 16. Buffer solutions in Chemistry are another example.

Ex. 17. A straight riverbed being a genuinely contrastatic system, it requires engineering works in order to be maintained.

Mutual relations of the two definitions and their connections with the general principles of Physics

As has been shown, it is possible to formulate a general definition of *equilibrium* expressed in variational conditions (1) and (2) and an operational definition of *stability* linked with the Le Chatelier-Braun principle. Is there any interdependence if not equivalency between the two definitions?

Though we are entitled to consider systems satisfying condition (1) as being in indifferent equilibrium for infinitesimal changes of the parameter[1], this is of little use as finite disturbances are likely to occur. Now we can in most cases foresee the behaviour of systems in such circumstances if we know the kind of extremum in (2), the occurring functions being analytical and mostly of simple character. Inversely, using the biological principle, we can expect that actual, viz. autostatic systems do, with suitably chosen parameters, satisfy conditions (1) and (2) or, at least, one of them. Contrastatic systems would obviously display the same property if they could only exist, since equations (1) and (2) hold for every kind of extremum. Now, as we pointed out, the finding of the suitable determining function requires a detailed knowledge of the system, whereas the application of the L. Ch.-B. principle seems always possible.

To complete our investigation of the relationship of the two definitions, let us present their logical sources. It appears clearly that the root of the L. Ch.-B. principle is nothing else but the principles of conservation and degradation of energy. To change the value of a parameter by a finite amount, external work must be done on the system, otherwise the system could change on its own accord and would not be stationary. The energy thus invested cannot perish and must result in an opposite move of the system, owing to the biological principle. We deduced, on the other hand, the variational definition as a generalisation of J. Bernoulli's principle of virtual displacement. This principle belongs with d'Alembert's principle, Lagrange's and Hamilton's equations, Newton's laws and Maupertuis-Hamilton's principle of least action to a chain of relations on which the whole of Mechanics is based.[2] The principle of conservation of energy follows explicitely from Lagrange's and Hamilton's equations. Implicitely it forms the necessary logical background for all connections of the chain. So it also constitutes the common root of both the definitions of equilibrium and stability.

Let us now consider the connection between the principle of Le Chatelier-Braun and the II principle of Thermodynamics. Taking a formula like that of Clapeyron-Clausius, we can easily understand that it results from a Carnot-process, performed on the two phases or, more generally, two states of the given system. At this stage the I principle of Thermodynamics only is involved and, without reference to experiment, we are unable to foresee what the signs of the different entities may be. From the point of view of the I principle alone, the vapour tension could as well rise as fall with the temperature, the heat could be generated or absorbed in the process of evaporation and so on. This can be seen still better in the case of solubility. (Ex. 12.) But the position changes at once if the II principle is taken into consideration. Then the signs of the entities become interdependent otherwise spontaneous processes, increasing temperature-differences without compensation, could take place. So we can state that, as far as thermodynamic systems are concerned, the Le Chatelier-Braun Principle is in harmony with the II principle of Thermodynamics. But the position is different in Mechanics (Ex. 1—3) and those other sciences where the L. Ch.-B. principle seems valid, although these by far exceed the domain of Thermodynamics. Then the principle must be based on the more general principles of Energetics, viz. those of Conservation and Degradation of Energy.

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[1] OSTWALD, l. c., p. 251.

[2] GEIGER & SCHEEL, Hdb. d. Physik Vol. V, Ch. 2.

This admitted, two questions arise:

1. Are there in realms of Biology, Economics, etc. entities essential, behaving like energies, viz. following the laws of Energetics, or
2. is the Biological principle, as mentioned before, in fact equivalent to the II principle of Thermodynamics, or more general, of Energetics?

Whatever the answer to these questions may be, it shall be of great importance for the future development of Science.

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SUMMARY

A scheme comprising: 1) a variational definition of equilibrium based on the invariancy of a determining function for infinitesimal changes of a parameter and 2) an operational definition of stability, brought in connection with the Le Chatelier-Braun principle, founded on the reaction of the system against finite external interference, is considered. The history of the principle of Le Chatelier-Braun is briefly related and a biological principle as necessary complement introduced. Applications of the scheme are illustrated and analysed on a number of examples. The phenomena of natural and artificial stabilisation are discussed. Mutual relations of the two definitions and their connections with the principles of Mechanics and Thermodynamics and the doctrine of energetics are shown briefly.

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